Microwave Spectra of Furazan

II. Nuclear Quadrupole Coupling in d_1-Furazan

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The nuclear quadrupole coupling constants for the two nitrogen atoms in monodeuterated furazan (C_2HDN_2O) were determined from the hyperfine structure of eight rotational transitions with low J-values. The coupling constants along the inertial axes are:

$$\chi_{aa}(2) = +3.546(10)\,\text{MHz}, \quad \chi_{aa}(5) = -5.044(10)\,\text{MHz},$$
$$\chi_{bb}(2) = -4.690(10)\,\text{MHz}, \quad \chi_{bb}(5) = +3.900(10)\,\text{MHz},$$
$$\chi_{cc}(2) = +1.144(10)\,\text{MHz}, \quad \chi_{cc}(5) = +1.144(10)\,\text{MHz}.$$

In conjunction with structural information from the preceding study, these data yield the principal coupling constants, with 3σ-uncertainties, as:

$$\chi_R(2/5) = -5.53(4)\,\text{MHz},$$
$$\chi_T(2/5) = +4.39(4)\,\text{MHz},$$
$$\chi_\pi(2/5) = +1.14(4)\,\text{MHz}.$$

The radial electric field gradients deviate from the direction of the external bisector of the ring angle ONC by 24.6° towards the oxygen atom.

These results are in qualitative agreement with previous work by NQR spectroscopy and with the results of *ab initio* molecular orbital calculations.

I. Introduction

Some time ago, Redshaw, Palmer and Findlay [1] tested the capability of *ab initio* molecular orbital calculations (MOCs) by comparing the computed nuclear quadrupole coupling constants (NQCCs) of nitrogen in oxygen or sulphur containing heterocyclics (including furazan) with the experimental data, which were available from nuclear quadrupole resonance (NQR) and microwave spectroscopy (MWS). They found 'excellent levels of agreement' between theory (MOCs) and experiment (NQR, MWS) in the case of all those compounds for which the principal NQCCs, χ_R, χ_T and χ_π [2], had also been determined by MWS (Ref [1], Table 5). For furazan, experimental values of the principal NQCCs from MWS were not available for comparison since Saegebarth and Cox [3] had determined the NQCCs χ_{aa}, χ_{bb} and χ_{cc} along the inertial axes only, leaving magnitude and orientation of the principal NQCCs undetermined. For this reason Redshaw, Palmer and Findlay did not quantitatively compare the MWS data with their own results.

The described deficiency of the MWS data however does not preclude a test of their compatibility with MOC and NQR results. For such a test one may either transform the principal NQCCs χ_R and χ_T, as given by MOCs and NQR, to the direction of the inertial axes for comparison with χ_{aa} and χ_{bb}, or one may transform the MWS values from the inertial axes to the direction of the principal axes of the coupling tensor for comparison with the MOC and NQR values of χ_R and χ_T. Either transformation [4] merely requires knowledge of the angle θ_1 between the inertial axes and the principal axes of the coupling tensor (see figure with Table 1). As the MOCs provide the angle $\theta = 32.5°$ between χ_R and the bisector of the angle ONC, while the structure study of the preceding paper [5] yields $\theta_2 = 18.3°$ for the angle between the bisector and the inertial axis a, one arrives at $\theta_1 = \theta + \theta_2 = 50.8°$.

The results of the two transformations, carried out with this angle, are given in Table 1. They reveal a rather large incongruity of the MWS data with the qualitatively compatible NQCC-values from MOCs and NQR.

Since it seemed impossible to discover whether the discrepancies of Table 1 arose from inaccurate MWS

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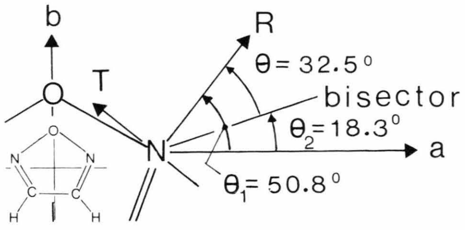
Table 1. Comparison of the nuclear quadrupole coupling constants (in MHz) of the nitrogen atoms in furazan, as determined from MOCs [1], NQR [1] and from MWS [3].



		χ_R	χ_T	$\chi_\pi = \chi_{cc}$
NQCCs along principal axes (R, T, π)	MOCs (computed)	−5.31	3.97	1.33
	NQR (experimental)	−4.656	3.492	1.164
	MWS (transformed)	−1.15	0.0	1.15
		χ_{aa}	χ_{bb}	$\chi_{cc} = \chi_\pi$
NQCCs along inertial axes (*a*, *b*, *c*)	MOCs (transformed)	+0.26	−1.60	1.33
	NQR (transformed)	+0.24	−1.40	1.16
	MWS (experimental)	−0.69	−0.46	1.15

data or from slightly incorrect values of χ_R, χ_T and θ, as given by MOCs and NQR, we considered it desirable to attempt the experimental determination of the principal NQCCs and of the angle θ_1 from a microwave investigation of the monodeuterated form of furazan. The rotation spectrum of this isotopic form shows considerably larger hyperfine splittings than the normal species, and it allows the evaluation of the principal NQCCs without reference to the NQCCs of any other isotopic form.

II. Experimental

a) Sample

Monodeuterated furazan (~ 60% enriched) was prepared as the perdeuterated species [5], the only difference being that a 3:2 mixture of D_2O (recovered from the previous preparation) and H_2O was used for the preparation of partially deuterated glyoxal sodium bisulphite.

b) Instrumental

The hyperfine splitting patterns of transitions of monodeuterated furazan were studied on a conventional, Stark-effect-modulated (SEM) spectrometer [6]. Free-running klystrons (OKI, EMI), allowing a minimum sweep speed of about 1 MHz/sec., were used as radiation sources. For best resolution only small microwave power levels were used and the sample pressure was held below 1 mTorr. Absorptions were displayed on the oscilloscope.

All splittings between hyperfine components were measured repeatedly, and different harmonics of the frequency standard were used deliberately. Final values of the splittings were obtained by averaging over individual results. On the two crucial $J = 0 \rightarrow 1$ transitions more than 20 independent measurements were taken on each hyperfine component.

III. Quadrupole Analysis

a) Background Aspects

It follows from the C_{2v} symmetry of furazan that the electronic environment of the nitrogen nuclei N(2) and N(5) are equal. The magnitudes of the principal NQCCs are therefore the same at both sites and the orientation of the in-plane gradients (χ_R, χ_T) with respect to the molecular symmetry axis are equivalent. For the microwave experiment which, in contrast to NQR does not normally yield the principal NQCCs but the electric field gradients in the direction of the inertial axes, this implies that $\chi_{ii}(2) = \chi_{ii}(5)$ for all isotopic forms in which the C_{2v} symmetry is preserved.

In considering the coupling situation for d_1-furazan it is assumed that the replacement of one hydrogen atom by deuterium will only destroy the symmetry of the mass distribution, but not the symmetry of the structure itself, nor that of the electron distribution within the molecule. The electronic environment of N(2) will therefore remain equal to that of N(5), and the orientation of the two quadrupole tensors with respect to the C_{2v} axis of the parent molecule will remain equivalent. The inertial axes of d_1-furazan, however, will be rotated from their directions in the symmetrical forms, and the *b*-axis will deviate from the C_{2v}-axis by an angle which can be calculated accurately from the structure data of the preceding paper [5] as $\alpha = 30.13°$. It follows that the *a*-axis in d_1-furazan (see Fig. 1) will deviate from the direction of χ_R (2) by 30.13° more than in the normal form, and it will deviate from the direction of χ_R(5) by 30.13° less than in the C_{2v}-symmetrical species. As a result, the two equal coupling tensors will give rise to different gradients along the *a*-axis of the monodeuterated

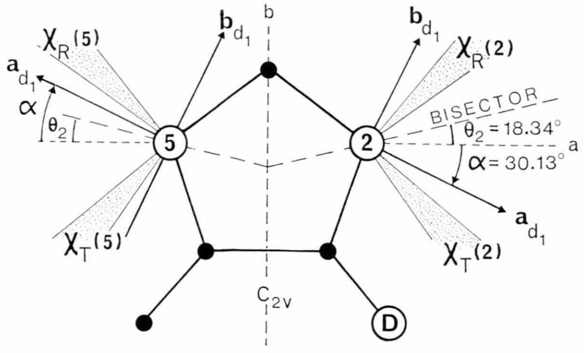


Fig. 1. Expected orientation of the principal NQCCs (dotted sectors) with respect to the inertial axes of normal furazan (dashed) and with respect to the inertial axes of d_1-furazan.

form ($\chi_{aa}(2) \neq \chi_{aa}(5)$), with analogous consequences for the gradients along the direction of the *b*-axis ($\chi_{bb}(2) \neq \chi_{bb}(5)$). The gradients in the direction of the inertial axis *c*, however, will not be affected by the rotation of the *a*- and *b*-axis, so that $\chi_{cc}(2) = \chi_{cc}(5) = \chi_\pi$, as in the C_{2v}-symmetrical forms.

It is clear from this exposition that the experimental determination of $\chi_{aa}(2)$, $\chi_{aa}(5)$, $\chi_{bb}(2)$ and $\chi_{bb}(5)$ from the hyperfine splittings in the spectrum of d_1-furazan provides the same type of information as the study of two isotopic species (with differently oriented inertial axes) in the case of a molecule with only one quadrupolar nucleus. In other words: Due to the equality of the coupling tensors around N(2) and N(5) the values $\chi_{ii}(2)$ and $\chi_{ii}(5)$ of monodeuterated furazan can be looked upon as the field gradients around a single nucleus, measured along two *a*- and two *b*-directions which differ from each other by $2\alpha = 60.26°$. Since such data allow the evaluation of the off-diagonal coupling constant χ_{ab}, one arrives at the not too frequent situation that the magnitude as well as the orientation of the principal NQCCs in furazan can be deduced from the study of a single isotopic form.

b) Spectroscopic Results

The analysis of hyperfine splittings (hfs) in the spectrum of d_1-furazan started with the estimation that the deviation of χ_R from the ONC bisector towards the oxygen atom would not be much less than in isoxazole [7] ($\theta = 26.1°$) and not much more than indicated by the MOCs [1] ($\theta = 32.5°$). Accordingly, the directions of χ_R and χ_T were expected within the 'dotted' sectors of Fig. 1 and, unless both MOC and NQR results were seriously in error, they should have values of $\chi_R \simeq -5$ MHz and $\chi_T \simeq +4$ MHz. It followed that, in the crudest approximation, $\chi_{aa}(2) \simeq \chi_{bb}(5) \simeq \chi_T \simeq +4$ MHz and $\chi_{bb}(2) \simeq \chi_{aa}(5) \simeq \chi_R \simeq -5$ MHz.

For numerical refinement of these initial estimates, the spectroscopic efforts were focused first on the two $J = 0 \rightarrow 1$ transitions. The hfs of the $0_{00} \rightarrow 1_{11}$ transition at ~14903 MHz (Fig. 2a) depend only on the two χ_{bb}-values (rather than on all four in-plane NQCCs), and those of the less intense $0_{00} \rightarrow 1_{01}$ transition at 13880 MHz (Fig. 2c) depend only on the two χ_{aa}-values. Both transitions are well resolved into quintet patterns, and the asymmetry of these indicates that $\chi_{bb}(2) \neq \chi_{bb}(5)$ and that $\chi_{aa}(2) \neq \chi_{aa}(5)$. For such a case, the central component of each quintet consists of a narrow triplet, while the other four components arise from single transition frequencies. For this reason, measurements were concentrated on the splitting L between the two low-frequency components, on the splitting I between the two components adjacent to the central peak, and on the splitting H between the high-frequency components of each quintet.

To extract the χ_{bb}-constants from the measured splittings L, I, and H of the $0_{00} \rightarrow 1_{11}$ transition, the hfs were computed [8] for χ_{bb}-combinations in the range $-5.5\,\text{MHz} < \chi_{bb}(2) < -3.5\,\text{MHz}$ and $3.0\,\text{MHz} < \chi_{bb}(5) < 5.0\,\text{MHz}$. Once a comparison between measured and calculated splittings had shown that the χ_{bb}-combination which simultaneously reproduces all three measured splittings occurred near $\chi_{bb}(2) = -4.7$ MHz and $\chi_{bb}(5) = +3.9$ MHz, the stepwidth of the model calculations was reduced to 0.05 MHz and χ_{bb}-combinations compatible with the measured values of L, I and H individually were plotted. The result is reproduced as Fig. 2b, from which $\chi_{bb}(2) = -4.685$ MHz and $\chi_{bb}(5) = 3.900$ MHz are seen to give an excellent match of all three measured splittings. – The hfs of the weaker $0_{00} \rightarrow 1_{01}$ transition (Fig. 2c) were analysed in the same way, giving $\chi_{aa}(2) = 3.522$ MHz and $\chi_{aa}(5) = -5.054$ MHz. Figure 2d shows that the match of the three splittings is not as perfect as in the case of the b-type transition. This is the consequence of the occurrence of a weak transition (vibrational satellite) very close to the lowest hyperfine component.

The diagrams of Fig. 2b,d indicate that uncertainties of ±0.01 MHz in the measured splittings of the $J = 0 \rightarrow 1$ transitions do not allow the determination of the coupling constants to better than ±0.02 MHz, and a discrepancy of that order of

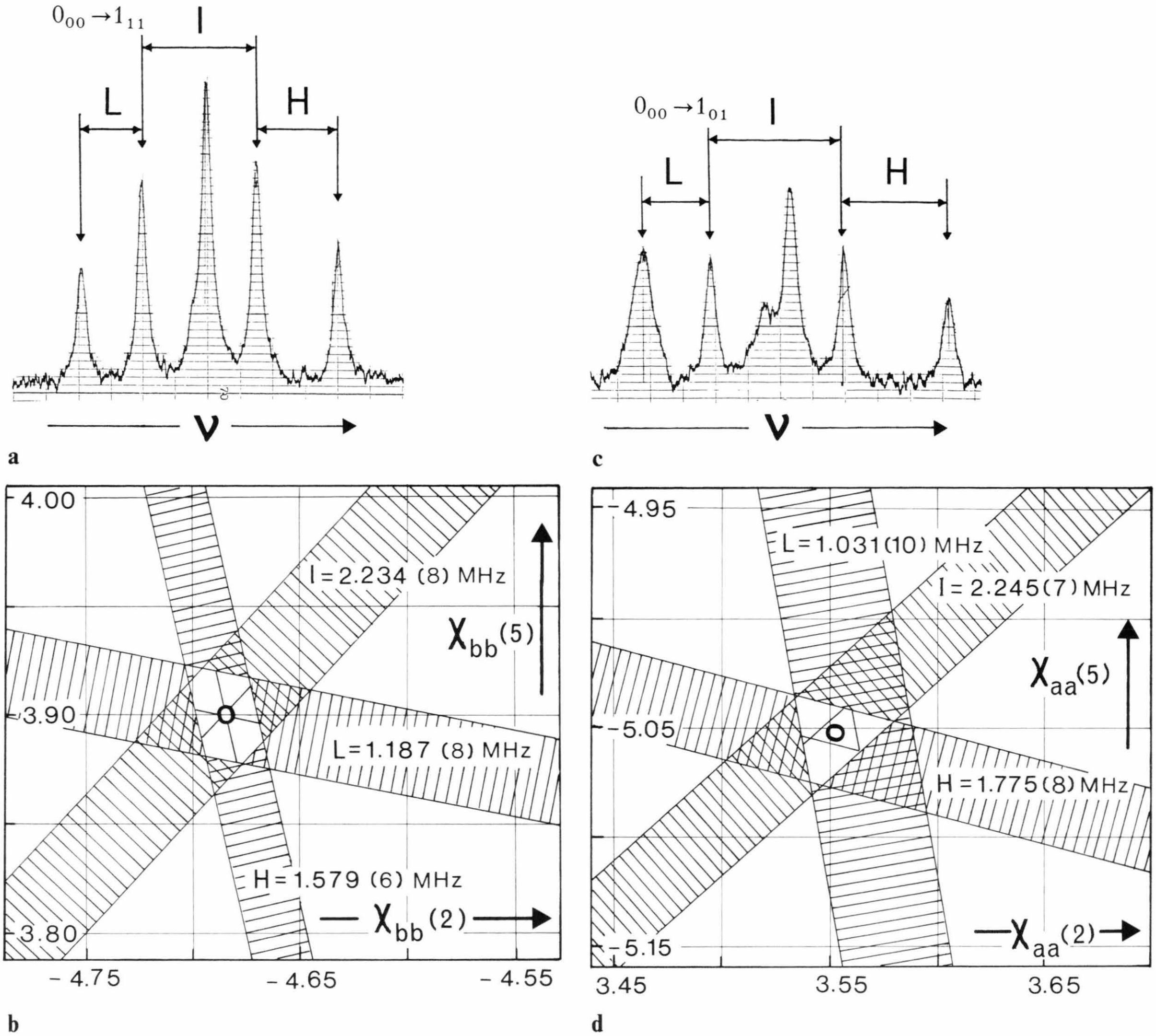


Fig. 2. **a**) The *b*-type $0_{00} \rightarrow 1_{11}$ transition at ~14903 MHz. **b**) Plot of χ_{bb}-combinations compatible with the measured hyperfine splittings L, I, and H. **c**) The *a*-type $0_{00} \rightarrow 1_{01}$ transition at ≃13880 MHz. **d**) Plot of χ_{aa}-combinations compatible with the measured hyperfine splittings L, I, and H of the *a*-type transition.

Table 2. NQCCs in monodeuterated furazan (in MHz).

		N(2)	N(5)
From $J = 0 \rightarrow 1$ transitions alone	χ_{aa}	3.552(25)	−5.054(20)
	χ_{bb}	−4.685(15)	3.900(15)
	χ_{cc}	1.133	1.154
From LSQ-fit of 87 measured splittings	χ_{aa}	3.552 (8)	−5.047 (7)
	χ_{bb}	−4.690 (8)	3.897 (9)
	χ_{cc}	1.138	1.150
Adopted values	χ_{aa}	3.546(10)	−5.044(10)
	χ_{bb}	−4.690(10)	3.900(10)
	χ_{cc}	1.144(10)	1.144(10)

magnitude in the two equal χ_{cc}-values has to be expected (Table 2, row 3).

In an attempt to refine further the accuracy of the NQCCs, and the consistency of the χ_{cc}-values in particular, the four R-branch transitions $1_{01} \rightarrow 2_{02}$ ~ 24313 MHz, $1_{11} \rightarrow 2_{12}$ ~ 23451 MHz, $1_{01} \rightarrow 2_{12}$ ~ 24475 MHz and $1_{11} \rightarrow 2_{02}$ ~ 23290 MHz and the two Q-branch transitions $3_{22} \rightarrow 3_{31}$ ~ 17622 MHz and $5_{41} \rightarrow 5_{50}$ ~ 15784 MHz were studied in detail: With fixed χ_{bb}-values the hfs of each of the six transitions were computed for χ_{cc}-constants of 1.10 MHz and 1.40 MHz and 37 splittings sensitive to the variation of χ_{cc} were compared with their experimental counterparts. This yielded χ_{cc}-values ranging from 1.12 MHz to 1.18 MHz. While these results confirmed the value derived from the $J = 0 \rightarrow 1$ transitions alone, an improvement of the accuracy of χ_{cc} was clearly not to be achieved in this way. This failure is ascribed to the fact that there hardly occur hyperfine components which can be assigned to a single resolved transition for $J > 1$. – The 87 measured splittings were therefore inserted into a least-squares (LSQ) fitting program [9] of hyperfine transitions. This reduced the uncertainties of the in-plane coupling constants to below 0.01 MHz, with a simultaneous improvement of the consistency of the χ_{cc}-values to 0.012 MHz. The average χ_{cc}-value derived from the LSQ-fit coincides with that of the fit of the $J = 0 \rightarrow 1$ transitions alone, and this justifies the adoption of the mean value of $\chi_{cc} = 1.144$ MHz, which requires only minute adjustments of the χ_{aa}-values for internal consistency ($\Sigma \chi_{ii} = 0$).

The NQCCs deduced from the $J = 0 \rightarrow 1$ transitions alone are compared with those obtained from the LSQ-fit in Table 2, which also gives the χ-values adopted for the subsequent evaluation of the principal NQCCs.

c) *Principal NQCCs*

As outlined in Sect. *a*, above, the two sets of in-plane coupling constants of row 7 and 8 of Table 2 may be looked upon as the NQCCs of N(2), measured first along the inertial axes of the 3-d$_1$-species ($\chi_{ii}(2)$-values correspond to the NQCCs of the 'parent' form) and then along the axes of the 4-d$_1$-species ($\chi_{ii}(5)$-values represent the NQCCs of N(2) along the axes of a 'substituted' species). Alternatively, the data may be treated as the NQCCs of N(5), measured first along the inertial axes of the 3-d$_1$-form and then along the axes of the 4-d$_1$-species. In either case, the orientation of the inertial axes in the 'parent' and the 'substituted' form differs by $2\alpha = 60.26^\circ$ [5], and the off-diagonal coupling constants χ_{ab} may therefore be evaluated [4] as

$$\chi_{ab}(2) = +2.764\ \text{MHz} \quad \text{and} \quad \chi_{ab}(5) = -2.144\ \text{MHz}.$$

These χ_{ab}-values, in turn, allow the deviation θ_1 of the radial field gradient χ_R from the direction of the inertial axis *a* of 3-d$_1$-furazan to be deduced as

$$\theta_1^{3\text{-d}_1}(2) = 73.07^\circ \quad \text{and} \quad \theta_1^{3\text{-d}_1}(5) = -12.81^\circ.$$

In conjunction with the structural information [5], these values imply that χ_R deviates from the inertial axis *a* of the normal form of furazan by

$$\theta_1^{\text{normal}} = 73.07^\circ - 30.13^\circ = 12.81^\circ + 30.13^\circ = 42.94^\circ,$$

and therefore by

$$\theta = 42.94^\circ - 18.34^\circ = 24.60^\circ$$

from the ONC-bisector towards the oxygen atom.

From standard relations [4], together with either $\theta_1^{3\text{-d}_1}(2)$ or $\theta_1^{3\text{-d}_1}(5)$, the principal NQCCs finally emerge as

$$\begin{aligned} \chi_R(2/5) &= -5.531\ \text{MHz}, \\ \chi_T(2/5) &= 4.387\ \text{MHz}, \\ \chi_{cc}(2/5) = \chi_\pi(2/5) &= 1.144\ \text{MHz}, \end{aligned}$$

with 3σ-uncertainties below 0.04 MHz. With these values for the principal NQCCs, the asymmetry parameter η is calculated as

$$\eta = (\chi_\pi - \chi_T)/\chi_R = 0.5863.$$

d) *Quadrupole Coupling in other Isotopic Forms*

In combination with the rotation of inertial axes under isotopic substitution, which can be calculated with good precision from the results of the preceding structure study, knowledge of the magnitude and orientation with respect to the molecular geometry of the principal NQCCs allows the evaluation of the coupling constants along the inertial axes of all isotopic forms of furazan. The results of such calculations are presented in Table 3. They allowed the prediction of hyperfine patterns in the spectra of the isotopic forms reported in the preceding paper [5]. Comparison of the predicted patterns with the observed splittings gave quantitative agreement not only for the normal form and the 3,4-d$_2$-species, but also for the two ^{13}C-forms.

IV. Discussion

The *assumptions* of Sect. III-a, concerning the preservation of structural and electronic symmetry in monodeuterated furazan, are probably not strictly fulfilled. The structure study [5] seems to contain a faint hint that slight distortion of the geometry does occur under deuteration. The assumptions also ignore the small quadrupole moment of deuterium, which will

Table 3. In-plane coupling constants of the nine isotopic forms of furazan utilized in the structure study [5].

Species[a]	Rotation of inertial axes	Angle between rad. gradient and inertial axis a	Coupling constants (in MHz)			
			$\chi_{aa}(2)$	$\chi_{bb}(2)$	$\chi_{aa}(5)$	$\chi_{bb}(5)$
Normal	0	$\theta_1(2/5) = 42.9°$	−0.93	−0.22	−0.93	−0.22
^{13}C(3)	5.3°	$\theta_1(2) = 48.2°$ $\theta_1(5) = 37.7°$	−0.02	−1.13	 −1.83	 +0.68
^{15}N(2)	3.8°	$\theta_1(5) = 46.8°$			−0.27	−0.88
^{18}O	0	$\theta_1(2/5) = 42.9°$	−0.93	−0.22	−0.93	−0.22
3-d$_1$[b]	30.1°	$\theta_1(2) = 73.1°$ $\theta_1(5) = 12.8°$	+3.55	−4.69	 −5.04	 +3.90
3,4-d$_2$	0	$\theta_1(2/5) = 48.2°$	−0.93	−0.22	−0.93	−0.22
^{13}C(3)-3,4-d$_2$	19.0°	$\theta_1(2) = 62.0°$ $\theta_1(5) = 23.9°$	+2.20	−3.34	 −3.90	 +2.76
^{15}N(2)-3,4-d$_2$	7.4°	$\theta_1(5) = 50.3°$			+0.34	−1.49
^{18}O-3,4-d$_2$[c]	90.0°	$\theta_1(2/5) = 47.1°$	−0.22	−0.93	−0.22	−0.93

[a] The isotopic forms are listed in the sequence of Table 2 of the structure study [5].
[b] NQCCs determined in this study.
[c] The inertial axes a and b are interchanged.

Table 4. Nuclear quadrupole coupling constants (in MHz) of furazan, as determined by MOCs, NQR and MWS.

	Method	θ	θ_1	χ_R	χ_T	$\chi_\pi = \chi_{cc}$
NQCCs along principal axes (R, T, π)	MOCs	32.5°	50.8°	−5.31	+3.97	+1.33
	NQR	–	–	−4.66	+3.49	+1.16
	MWS	24.6°	42.9°	−5.53	+4.39	+1.14
				χ_{aa}	χ_{bb}	$\chi_{cc} = \chi_\pi$
NQCCs along inertial axes (a, b, c)	MOCs transf'd	24.6°	42.9°	−1.00	−0.34	+1.34
	NQR transf'd	24.6°	42.9°	−0.87	−0.29	+1.16
	MWS			−0.93	−0.22	+1.14

couple unequally with the two nitrogen atoms. However, both these effects should be very small indeed and it is not thought that the small discrepancy in the χ_{cc}-values of N(2) and N(5) (Table 2, rows 3 and 6) could be a reflection of these effects, nor that the assumptions significantly affect the values of the NQCCs.

It is obvious from Fig. 2b, d that the *uncertainties* of the coupling constants remain of the same order of magnitude as the experimental uncertainties in the splittings from which they are determined. While four of the five components of the $J = 0 \rightarrow 1$ quintets arise from a single hyperfine frequency, there rarely occurs such a situation for higher J-values. Resolved hyperfine components then consist nearly always of two or more unresolvable transitions. Measured peak frequencies can therefore not be expected to coalesce to better than a few hundredths of a MHz with the hyperfine transition to which they must be primarily assigned. It follows, that an improvement of the accuracy of the deduced χ-values beyond 0.01 MHz can not be expected from the inclusion in the LSQ-fit of more hyperfine splittings from transitions with $J > 2$. For this reason we desisted from a detailed analysis of the other 91 transitions which were measured to ± 0.05 MHz in the course of the structure study. This seemed to be justified also by the fact that the hfs pattern of all those transitions agreed within experimental accuracy with that expected from the constants of Table 2.

The magnitude of the *principal NQCCs* and the direction of the gradients, given in Sect. III-c, and the revised coupling constants along the inertial axes of C_{2v}-symmetrical forms of furazan, given in Table 3, are the essential results of the present study. They answer the questions outlined in the introduction, and they allow Table 1 to be revised to Table 4. From rows 1 and 3 of that table it is seen that the magnitude of χ_R and χ_T derived by *ab initio* calculations agree to better than 10% with the MWS values, while the NQR results for both in plane NQCCs are about

0.9 MHz (~ 25%) smaller than the MWS values. – In the direction of the inertial axes the NQCCs deduced by MOCs, NQR and MWS remain as incompatible as in Table 1 if the MOC-value for θ (32.5°) is used in the transformation from principal to inertial axes. However, if the MWS-value of $\theta = 24.6°$ is used together with $\theta_2 = 18.3°$ (see figure with Table 1), the three sets of χ-values agree satisfactorily, with NQR data being closer to the MWS results than the χ-values from MOCs.

Since the previous MWS-values for χ_{aa} and χ_{bb} (-0.69 MHz and -0.46 MHz) are qualitatively confirmed by the present work, it follows that the discrepancy which prompted this investigation was produced primarily by the incorrect MOC value of θ, rather than by drastic inaccuracies of the data of Saegebarth and Cox [3]. While the angle θ is under-predicted by up to 5° by the MOCs for all other compounds considered in [1], it is over-predicted by as much as 8° in the present case of furazan. Unfortunately, we are not in a position to assess how much of this error in the MOC would be removed if the revised geometry of furazan (Part I) were used as starting point for the *ab initio* calculation.

A comparison between the present and the *previous values* for the coupling constants of normal furazan shows full agreement in $\chi_{cc} = \chi_\pi = 1.14$ MHz, but the in-plane constants are modified by ± 0.24 MHz. Although these corrections are about twice as large as the uncertainties quoted in the earlier work, the results of Saegebarth and Cox remain impressive when their unfortunate choice of the isotopic form, the small splittings of the transitions which they studied, and the instrumental facilities of their time are considered.

A discussion of the NQCCs and the structure of furazan in terms of *orbital populations*, as formulated initially by Lucken [10], does no longer seem appropriate, since this question should be answerable quantitatively on the basis of present day quantum-chemical calculations.

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